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REMOVAL OF NO_x POLLUTANT BY CATALYTIC COMBUSTION REACTIONS

F. SOLYMOSI AND J. KISS
Gas Kinetics Research Group, The University, Szeged, Hungary

Kinetic measurements have been made for the oxidation of CO, C_2H_4, H_2 and natural gas by nitric oxide on SnO_2/Cr_2O_3 and on Al_2O_3/Cr_2O_3 catalysts. The interaction of NO with catalysts was examined by adsorption, infrared spectra and electric conductivity measurements.

The adsorption isotherms of NO on SnO_2/Cr_2O_3 catalysts are of the Freundlich type in the pressure range from 3 to 50 Torr. Evaluation of the NO chemisorption rate by the Elovich equation yielded two linear segments with a distinct break between them. The instantaneous adsorption of NO on the partially reduced SnO_2 was larger than that of the unreduced sample. The rate of adsorption was ten times higher. A very large increase in the amount of adsorbed NO was obtained by adding Cr_2O_3 to SnO_2. Electric conductivity measurements during NO adsorption revealed that both negatively and positively charged NO are present on pure and doped SnO_2.

The catalytic reactions on pure SnO_2 occurred only above 400°C. Small amounts of Cr_2O_3 in the SnO_2 lowered the reaction temperatures by 100–200°C. The efficiency of SnO_2/Cr_2O_3 exceeded that of Al_2O_3/Cr_2O_3.

It is suggested that on the partially reduced SnO_2 the Sn^{3+} ions are the active catalytic sites for NO and that nitric oxide dissociates upon chemisorption. The slowest step of the reduction of NO is assumed to be the oxidation of reduced centers on the catalyst, which involves the formation of nitrogen molecules. The high activity of catalysts containing chromium oxide is attributed to the chromium ions incorporated into the surface layer of the carrier which can easily be reduced by fuels and rapidly reoxidized by NO.

Introduction

In recent years, concern over our environment has led to substantial action in all industrialized countries. A major environmental concern is that of air pollution. Catalytic combustion processes play an important role in combating environmental pollution caused by chemical plants and automobiles. Thanks to the vast amount of basic research on the oxidation of CO and hydrocarbons, the development of CO–CH catalysts for car exhaust gases is in an advanced stage. The state of development of NO catalysts, however, is far less advanced and requires more fundamental research.

The simplest way for the removal of nitric oxide formed in various combustion reactions would be its catalytic decomposition. Unfortunately the decomposition rates of nitric oxide on different types of catalysts are much too low to be of practical use.[1,2] The catalytic reduction of nitric oxide with CO offers an attractive means for eliminating this pollutant from car exhaust. The study of this reaction has been the subject of many recent papers but only a few of them are concerned with the reaction mechanism.[3,4]

It was found that the oxidation and reduction of the catalyst surfaces play an important role in the combustion reaction. Therefore our attention turned to catalyst systems that especially favor the redox reactions. A prominent catalyst in this respect is SnO_2 containing a small amount of added chromium oxide. The present work was undertaken to examine the interaction of nitric oxide with these catalysts and to investigate the kinetics and mechanism of the catalytic reduction of nitric oxide by different reducing agents.

Experimental

Materials

Cr_2O_3 was reagent grade material from Reanal. It was fired at 700°C for 5 h. Al_2O_3 was from

Degussa. The Al_2O_3–Cr_2O_3 catalyst was prepared by impregnating alumina with an aqueous solution of CrO_3. The gel was dried in air for 16 h at 120°C. For catalytic investigations, the powder was calcined for 8 hours at 600°C.

SnO_2 was obtained by the action of HNO_3 on metallic Sn. It was dried at 120°C, and heated at 350°C for 3 h and at 500°C for 5 h. The doping of the SnO_2 with Cr_2O_3 was effected in the following way:[5,6] Cr_2O_3 was added to an aqueous suspension of SnO_2 and after a sufficiently long period of stirring, the homogeneous suspension was dried and heated at 350°C for 5 h. Final sintering was performed at 900°C for 5 h in air.

The nitric oxide (Matheson Company) was commercially pure (99%). Ethylene was a product of Fluka Gmbh. Both gases were purified by bulb-to-bulb distillation before use. Carbon monoxide was prepared in the laboratory by reaction between formic acid and sulphuric acid at 83°C.

For the catalytic studies, small pellets (1.5 mm diam and 1.5 mm long) were made. A fixed amount of catalyst (1.5 g, 8–10 small pellets) was used in all experiments.

Methods of Measurements

For the kinetic investigations, a closed circulation system (volume 277 ml) was used. The reactions were followed by measuring the pressure of the reacting gases. A Hewlett-Packard gas chromatograph connected to the reactor was used to analyze the reaction products.

Conductivity measurements during the adsorption and catalytic reaction were performed in the same reactor, using pellets of 8 mm diameter and 6–7 mm long. An ac bridge was used for these measurements.

The active oxygen content of the catalysts was determined by the Bunsen method. Specific surface areas were calculated from the adsorption of nitrogen at liquid nitrogen temperature.

Adsorption measurements were performed in a Sartorius microbalance. Infrared spectra were taken with a double beam IR spectrophotometer (Spectromom 2000). The discs of Al_2O_3/Cr_2O_3 were made by pressing the finely divided powder dried at 120°C to a thickness corresponding to 30 mg/m^2. The sample was degassed in vacuo at 10^{-4} Torr. Further treatment is described in the text.

Results and Discussion

Characterization of the Catalysts

SnO_2 is an *n*-type semiconductor. Its electric conductivity is due to donor levels that arise from defects such as impurity cations and anion vacancies.[7,8] The incorporation of a small amount of Cr_2O_3 into SnO_2 in air significantly changes the physical properties of SnO_2.[5,6]

On the other hand, the chromium ions also undergo a noteworthy change; part of them is oxidized to a higher valence and stabilized in the surface layer of SnO_2.

A remarkable feature of higher valence chromium in the surface layer of SnO_2 is that after its reduction with fuels it can easily be reoxidized even at low temperatures.

Characteristic data for different catalysts used in this work are summarized in Table I.

Adsorption Measurements

The adsorption of NO has been investigated on Al_2O_3/Cr_2O_3 catalyst,[9] but no studies have been made on SnO_2.

The characteristic feature of the adsorption of NO on diamagnetic oxides is its extreme slowness; the establishment of the adsorption equilibrium is very difficult. The adsorption of NO on SnO_2 activated at 400°C in vacuum is also slow, in spite of the fact that there is no experimental evidence for a substantial energy of activation. Adsorption isotherms and rates for NO were measured at 25–100°C. The data conform well to the Freundlich isotherms in the pressure range covered, as shown by a linear relationship between the logarithmic amount of adsorbed NO, q, and the logarithmic pressure, p. The Freundlich isotherm is defined by

$$q = cp^{1/n}$$

where the coefficients n and c are functions of temperature. The points of intersection of isotherms show that the amount of NO required for a monolayer (q_m) is 7.46 μmoles/g. The pressure which is necessary to achieve monolayer coverage is 74.2 Torr. The average value of H_m, which is a measure of the heat of adsorption, is 6.9 kcal/mole. Similar low values have been obtained by Shelef, *et al.*, on transitional metal oxides.[9–11]

The rate of adsorption of NO was evaluated by the integrated form of the Elovich equation

$$q = (2.3/\alpha)\log(t+t_0) - (2.3/\alpha)\log t_0$$

where $t_0 = 1/a\alpha$ is an integration constant. The Elovich plots consist of two linear segments with a distinct break between them. A possible explanation of the break is that two distinct populations of adsorption sites exist on the sur-

TABLE I

Characteristic data for different catalysts

Catalyst	Cr_2O_3 content mole%	Highest calcination temperature °C	Surface area m^2/g	Active oxygen %	Average valency of chromium*
Cr_2O_3	100	700	30.4	0.0224	3
SnO_2	—	900	5.81	—	—
SnO_2	0.01	900	6.12	0.0015	4.5
SnO_2	0.1	900	6.58	0.01	3.95
SnO_2	0.5	900	8.84	0.043	3.81
SnO_2	1.0	900	11.87	0.082	3.77
Al_2O_3	1.0	900	4.64		
Al_2O_3	5	600	70.0	1.0243	5

* Calculated on the basis of active oxygen content.

† This sample of Al_2O_3 was a Reanal product. The doping with Cr_2O_3 was similar to the case of SnO_2.

TABLE II

Parameters for the adsorption of gases at 100°C on $SnO_2+Cr_2O_3$ catalysts

	SnO_2		$SnO_2+1\%Cr_2O_3$	
	α_1 $[\mu mole/g]^{-1}$	q_0 $\mu mole/g$	α_1 $[\mu mole/g]^{-1}$	q_0 $\mu mole$
NO	7.5	1.0	1.15	3.3
O_2	1.856	2.875	3.072	3.25
CO	1.77	0.4	0.621	1.66
C_2H_4	4.025	0.714	2.3	0.71

q_0 = the amount of instantaneous adsorption, α is the slope of the first segment of the Elovich plots.

face. The temperature coefficient of the slopes of both segments is positive, indicating a *increase* in the adsorption rate with temperature.

On the partially reduced SnO_2 (with CO at 400°C for 60 min) the instantaneous adsorption of NO was almost six times larger than that of adsorption on unreduced samples. In addition the rate of adsorption at 100°C was about ten times higher. The chemisorption of NO on unreduced SnO_2 is reversible, whereas on SnO_2 reduced with fuels it was somewhat irreversible. In the latter case it is assumed that mainly oxygen remains on the surface, while NO is reduced to N_2O. A very large increase in the adsorbed amount of NO and in the rate of chemisorption was achieved by incorporating Cr_2O_3 (0.1–1 mole%) into the surface layer of SnO_2 (Table II).

Similar measurements were carried out for the adsorption of other gases, e.g., CO, O_2, and C_2H_4. The instantaneous adsorption of CO is commensurable with that of NO. The Elovich plots also consist of two intersecting straight line segments. While α_1 decreases with temperature, α_2 increases with T.

If we compare the adsorption of NO and O_2 on SnO_2, we find that both the extent of instantaneous adsorption of O_2 and the rate of subsequent adsorption are always larger than for NO. With the increase of adsorption temperature, this difference becomes greater.

The initial adsorption of ethylene on SnO_2 below 100°C has the highest value of all the gases (fuels) studied so far, it is however hardly affected by the increase of temperature or by incorporating chromium into SnO_2. Accordingly, near the reaction temperature, the adsorption of O_2 and NO greatly exceeds that of ethylene. Data for

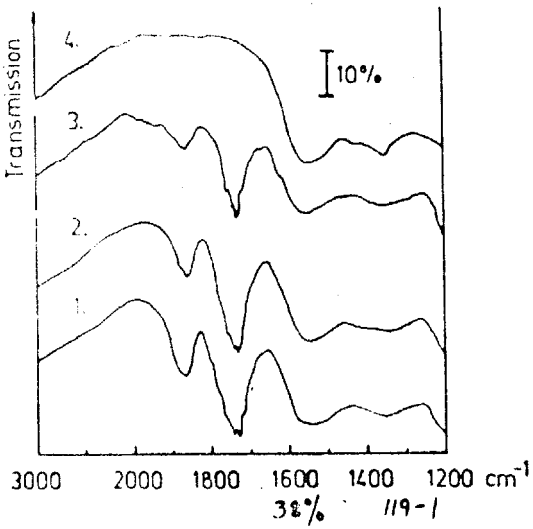

FIG. 1. Infrared spectra of NO on Al_2O_3/Cr_2O_3. Adsorption of NO (5 Torr) was carried out at 25°C for 1 h, then the sample was evacuated and heated at different temperatures for 30 min. All the spectra were taken at 25°C. The temperatures of heat treatment were the following: 1, 25°C; 2, 100°C; 3, 150°C; 4, background spectra.

adsorption of different gases on $SnO_2+Cr_2O_3$ catalysts are shown in Table II.

The coadsorption of NO+fuel and the effect of preadsorbed NO on the subsequent adsorption of fuel were studied at 100°C on SnO_2 activated in vacuo at 400°C. It appears that the preadsorbed nitric oxide promoted the adsorption of both carbon monoxide and ethylene. The ratio of the amount of adsorbed NO and that of adsorbed CO (promoted) approaches the value of 1, pointing to the existence of a surface complex comprising 1 mole NO and 1 mole CO. Promoted adsorption was also found on SnO_2 using a mixture of O_2 and C_2H_4.[12] However, on Al_2O_3/Cr_2O_3 catalysts no promoted adsorption was observed in either case.

*Infrared Spectroscopic Measurements**

Infrared studies have been reported of adsorption of NO on various oxides[1,13] and a great number of bands have been observed representing adsorbed NO species ranging from $(NO)_2$ dimer to adsorbed NO^+ and NO^- ions. There are however substantial contradictions on several important details in the various papers. It now seems certain that the transition metal ions are the primary adsorption centers and that bands observed between 1000–2000 cm^{-1} when NO is added to alumina or silica are due to the presence of transitional metal impurities.[14,15]

Unfortunately all our efforts to make transparent discs from SnO_2/Cr_2O_3 have been unsucessful, restricting our infrared studies to the Al_2O_3/Cr_2O_3 system.

When NO was added to Al_2O_3/Cr_2O_3, pretreated in CO (initial pressure 10 Torr) at 400°C for 1 h, two large bands appeared at 1865 and 1740 cm^{-1} (Fig. 1). The latter is perceptibly composed of a combination of separate bands at 1743 and 1738 cm^{-1}. Both bands have been observed recently during the adsorption of NO on Al_2O_3/Cr_2O_3 activated in ethylene.[16] Based on the assignments of NO bands observed on transition metal oxides,[13,17] the band at 1743 and 1738 cm^{-1} was attributed to NO covalently bound to Cr^{3+} and Cr^{5+} sites, respectively. The absorption band at ~1860 cm^{-2} was assigned to NO chemisorbed by a double bond ionic link ($Cr^{n+}=N^+=O$) to chromium ions $Cr^{(n+1)+}$. However, the observation that the intensities of both bands increased upon reduction at high temperatures—which resulted in extensive formation of Cr^{2+} on the surface—led to the assumption that these bands are due to NO adsorbed on Cr^{2+} ions.[18]

Further study is evidently needed to identify the adsorption sites and to choose between the alternatives. The marked difference found between the adsorptive properties of strongly and weakly reduced catalysts containing chromium supports the idea that the lower valence chromium ions are the primary adsorption sites for NO.[19]

In further study, it appeared that the band at 1860 cm^{-1} decreased in intensity with temperature and disappeared completely at 200°C. The band at 1740 cm^{-1} did not change up to 150°C, subsequently the intensity decreased and above 300°C this band was no longer discernible. With a gas mixture of NO+CO(1:1), only the bands due to adsorbed NO appeared on the spectra, although the adsorption of CO in the absence of NO yielded its characteristic bands.

The intensity of the bands due to adsorbed NO was slowly reduced when CO was added to the sample at 25–100°C, and depending on the temperature, the bands were completely eliminated. The rate of removal of the band at 1860 cm^{-1} was somewhat higher than that of the band at 1740 cm^{-1}. It is interesting that the bands due to adsorbed CO appeared neither during nor after the completion of the surface process. Taking into account that adsorbed NO is much more strongly bound than the adsorbed CO it may be assumed that the disappearance of these bands is due to the reaction between the adsorbed

* Infrared studies were made in cooperation with Dr. J. Raskó.

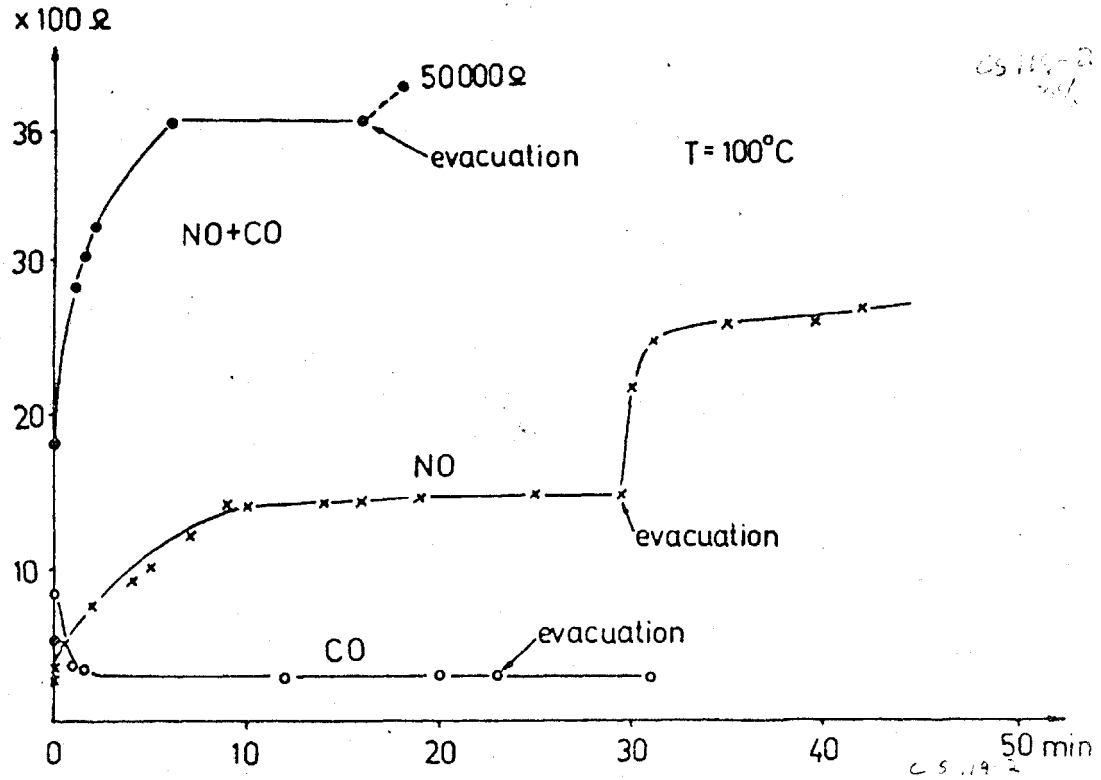

FIG. 2. The effect of NO, CO, and NO–CO mixture on the electric resistivity of SnO_2 activated at 400°C in vacuo. Temperature: 100°C.

NO and gaseous CO. When the sample was evacuated after the removal of NO bands and exposed again to NO at 25°C no reappearance of the bands at 1860 and 1740 cm^{-1} was experienced. This indicates that the surface centers for the adsorption of NO that yield bands at 1860 and 1740 cm^{-1} have been deactivated (oxidized) during the surface reaction.

Electric Conductivity Measurements During the Adsorption of NO *and* CO

Surprisingly little information is available concerning the electronic interaction of NO with solids and, to our knowledge, electric conductivity measurements have not been used yet to evaluate the interaction between NO and semiconducting oxides. The low ionization potential of NO (9.5 V) makes possible the conversion of the nitric oxide molecule to the positive nitrosonium ion [NO^+]. It can also easily take over an electron to be converted to a negative nitrosyl ion [NO^-], as there is no evidence of any barrier to electron attachment. The lower limit to electron affinity of gaseous NO is 0.65 eV.[20]

Figure 2 shows that adsorption of NO increases the electric resistivity of activated SnO_2. The electric resistivity of ZnO and TiO_2 changed in the same direction upon the adsorption of NO.[21]

This may indicate that the chemisorption of NO on *n*-type oxides is an acceptor process

$$NO_{(g)} + e_0^- = NO^-_{(chem)}. \qquad (1)$$

However, considering the recent spectroscopic investigations of Kortüm[22] on the adsorption of NO on ZnO, it is also possible that SnO_2 activated in high vacuum at 400°C is capable of reducing NO to N_2O at 100°C, according to the equation

$$2NO + e_0^- = N_2O + O^-. \qquad (2)$$

This process could also contribute to the increase in the electric resistivity of SnO_2.

It was interesting to observe that pumping off the NO from the reaction cell at the same temperature caused a further slight increase in the electric resistivity of SnO_2. This behavior was also observed for SnO_2 doped with 0.1 or 0.5

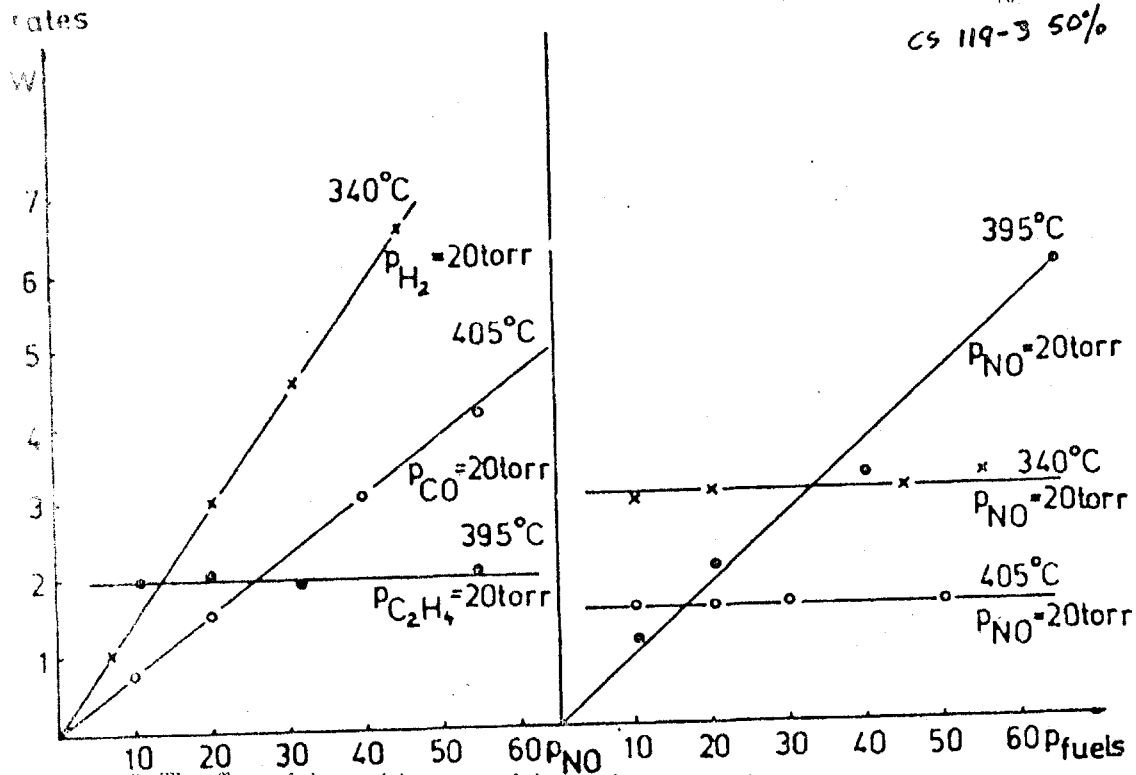

FIG. 3. The effects of the partial pressure of the reacting gases on the rates of NO-fuels reactions.

mole% Cr_2O_3. A tentative explanation is that, in addition to the above mode of adsorption, part of the NO may be chemisorbed by giving its unpaired electron to the oxide surface to form an apparently positive chemisorbed ion

$$NO_{(g)} = NO^+_{(chem)} + e_0^- . \qquad (3)$$

This kind of NO adsorption partly compensates the result of the electron acceptor adsorption of NO [Eq. (1)]. This adsorption is reversible or much weaker than the former, so that upon evacuation of the sample at 100°C, NO^+ desorbs from the surface

$$NO^+_{(chem)} + e_0^- = NO_{(g)} \qquad (4)$$

and as a result the electric resistivity of SnO_2 increases.

The electric resistivity of SnO_2 also increased when a mixture of NO and CO (1:1) was introduced onto the sample, in spite of the fact that CO alone decreases the resistivity of SnO_2

$$CO_{(g)} = CO_{(chem)}^+ + e_0^- . \qquad (5)$$

Kinetic Measurements

The reaction of CO with NO on SnO_2 activated at 400°C in vacuo proceeded at a measurable rate only above 390°C. After a slight decrease, the activity of the catalyst remained constant. With a stoichiometric composition, a steady state activity at this temperature was attained after 40–60 min. When CO was in excess, the reduction of nitric oxide to nitrogen was practically complete; the amount of nitrous oxide found remained below 1%. A slight activity of SnO_2 was also experienced at 180–360°C, but the conversion reaction was very low and the catalyst surface rapidly became poisoned.

The reaction was zero order with respect to CO, and first order with respect to NO. The activation energy was 36.6 kcal/mole, and thus considerably larger than that of the CO–O_2 reaction.[21]

The incorporation of a small amount of Cr_2O_3 into the surface layer of SnO_2 markedly increased the efficiency of SnO_2. On a catalyst containing 1% chromium oxide, the reaction between CO and NO proceeded at temperatures as low as 150°C. The value of the activation energy

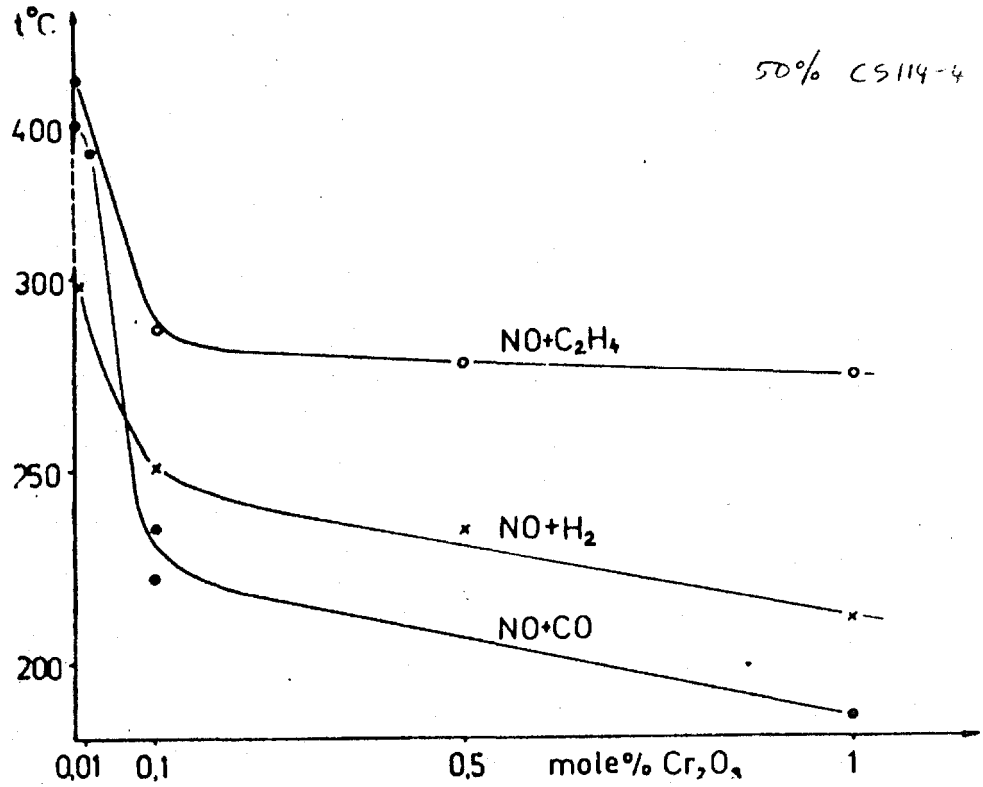

FIG. 4. Values of reaction temperatures at which the rate constant of the reactions is 1×10^{-3} sec^{-1} m^{-2}.

decreases with the increase of the amount of Cr_2O_3 in SnO_2.

The catalytic reaction between H_2 and NO on pure tin dioxide was measured at 320–360°C. It was somewhat faster than the NO–CO reaction under similar conditions. The formation of NH_3 was detected even in the presence of a slight excess of H_2 (H_2:NO mole ratio 2:1). Pure tin dioxide catalyzed the reduction of NO with ethylene only above 390°C. The sample doped with 1% chromium oxide lowered the temperature range of both reactions by about 100–150°C. Figure 3 shows the rate of the reduction of NO with different fuels as a function of the partial pressure of the reacting gases.

The catalytic efficiency of SnO_2 containing Cr_2O_3 has been tested in the reduction of NO with natural gas containing CH_4 (91.1%), C_2H_4 (1.46%), C_3H_6 (0.72%), C_4H_{10} (0.54%), C_5H_{12} (0.12%), CO_2 (2.74%), N_2 (3.37%). Undoped SnO_2 catalyzed the reaction only above 450°C. When 1% Cr_2O_3 was incorporated into SnO_2 the oxidation reaction between natural gas and NO occurred around 300°C. In the presence of excess natural gas, the reduction of NO to N_2 was complete at this temperature.

In order to compare the effect of the chromium content of SnO_2 on the reduction of NO with different fuels, the reaction temperatures, at which the rate constants of the reactions have a value of 1×10^{-3}, are shown in Fig. 4 as function of the chromium oxide content of the tin dioxide.

The addition of Cr_2O_3 to SnO_2 exhibited the largest effect in the case of NO+CO reaction.

For comparison, the reduction of NO has been investigated on pure Cr_2O_3 and on Al_2O_3/Cr_2O_3 catalysts. The latter was found to be one of the most active oxides in the reaction between NO and CO.[3]

Kinetic data for the reduction of NO are collected in Table III. These data show that SnO_2+Cr_2O_3 has the highest activity among the catalysts studied in this work in the low temperature reduction of nitric oxide.

A Possible Mechanism of Reduction of NO with CO

We may attempt now to formulate a mechanistic picture of the reaction mechanism. It seems certain that different active centers are responsible for the catalytic reactions on pure SnO_2

TABLE III

Kinetic data for the catalytic reduction of NO with different fuels

Reaction	SnO_2	$SnO_2+1\%Cr_2O_3$	Cr_2O_3	$Al_2O_3+1\%Cr_2O_3$	$Al_2O_3+5\%Cr_2O_3$
NO–CO reaction					
Temperature range, °C	405–440	170–205	215–300	318–360	220–263
Reaction order to NO	1	1	1	1	
Reaction order to CO	0	0	0	0	
k_{spec}, at 250°C	2.35×10^{-6}*	1.18×10^{-2}	5.04×10^{-4}	1×10^{-4}*	5.8×10^{-4}
E, kcal/mole	36.6	18.2	36.5	33.8	13.3
NO–C_2H_4 reaction					
Temperature range, °C	395–428	250–310	380–430	370–430	250–300
Reaction order to NO	0	0			
Reaction order to C_2H_4	1	1			
k_{spec}, at 250°C	7.4×10^{-6}*	4.7×10^{-4}	1.57×10^{-5}*	2.8×10^{-5}*	5×10^{-5}
E, kcal/mole	19.6	14.1	17.1	17.9	
NO–H_2 reaction					
Temperature range, °C	320–360	180–230			
Reaction order to NO	1	1			
Reaction order to H_2	0	0			
k_{spec}, at 250°C	1.84×10^{-4}*	5.08×10^{-2}			
E, kcal/mole	15.2	15.2			

* Extrapolated value.

$k_{spec} = [\text{mol}\cdot\text{min}^{-1}\text{m}^{-2}]$.

and on $SnO_2+Cr_2O_3$ catalysts. We may assume that in the case of undoped SnO_2, Sn^{3+} is the active catalytic site. This assumption is based on our observation that the activity of the catalyst in the chemisorption and reduction of NO is enhanced when it is partially reduced; the catalyst surface is oxidized and inactivated by NO.

From electric conductivity measurements during the adsorption of NO it was concluded that both negatively and positively charged adsorbed NO occurs on the SnO_2 surface. The formation of NO^- is very likely to occur through the transfer of a 5s electron of Sn^{3+} ion to NO

$$Sn^{3+}+NO_{(g)}\rightleftharpoons Sn^{4+}NO^- \qquad (6)$$

whereas the nitrosonium ion, NO^+, is formed due to the transfer of the odd electron from NO to the Sn^{4+} ion

$$Sn^{4+}+NO_{(g)}\rightleftharpoons Sn^{3+}NO^+. \qquad (7)$$

Electric conductivity measurements also indicated that NO^+ is much more weakly held on SnO_2 than NO^- ions. Since the formation of NO^+ is accompanied by the strengthening of the bond, whereas the transfer of an electron to the antibonding orbital of NO tends to weaken the N–O bond, it seems plausible to assume that the oxidation of the catalyst surface is due to dissociation of the NO^- species.

Accordingly the following steps are postulated for the reduction of NO by CO (M represents the active site, Sn^{3+}):

$$M+NO\rightleftharpoons M^+NO^- \qquad (8a)$$

$$M^+NO^-+M\rightarrow M-N+M^+O^- \qquad (9a)$$

or

$$M+NO\rightleftharpoons M-NO \qquad (8b)$$

$$M-NO+M\rightarrow M-N+M^+O^- \qquad (9b)$$

$$M-N+NO\rightarrow M^+O^-+N_2 \qquad (10)$$

$$M^+O^-+CO\rightarrow M+CO_2. \qquad (11)$$

The formation of N_2O may occur in the reaction

$$M-N+NO\rightarrow M+N_2O. \qquad (12)$$

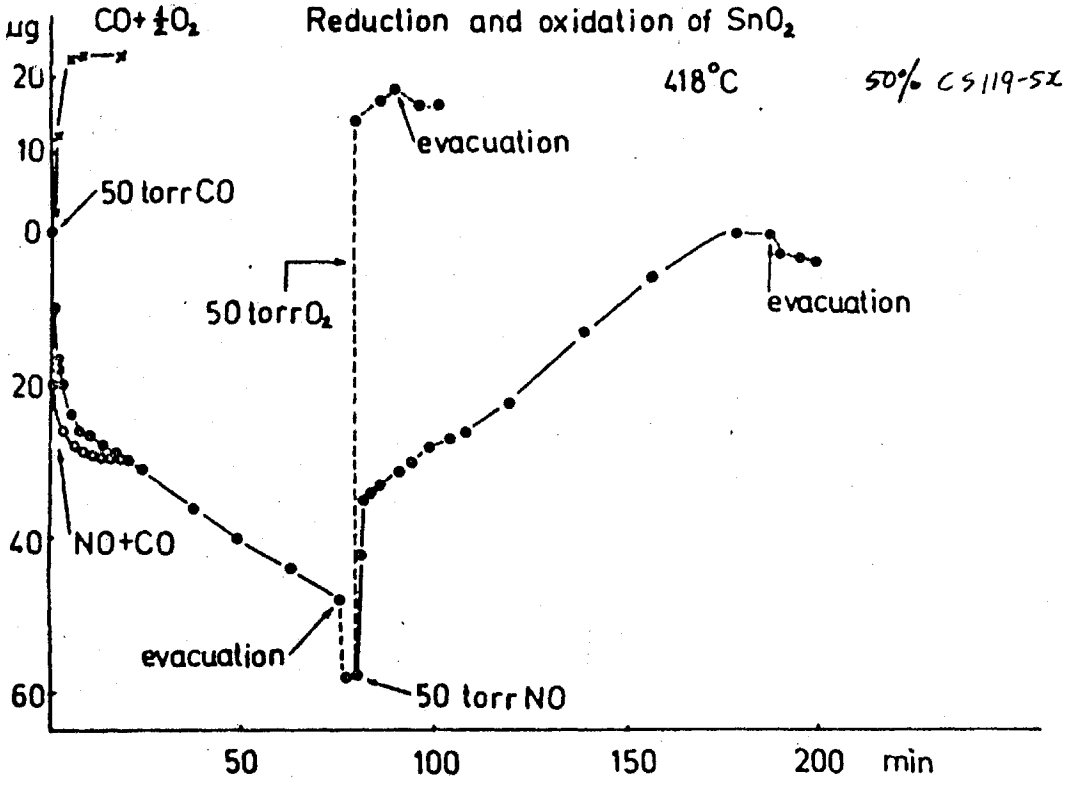

FIG. 5. Interaction of SnO_2 with NO, CO, NO+CO, and O_2+CO gas mixtures under reaction conditions at 400°C measured with a sensitive microbalance. The weight changes of the catalyst during the interaction with different gases are shown as ordinates.

An alternative to reactions (10) and (11) is that CO reacts with the adsorbed nitrogen atom

$$M\text{-}N+CO \rightleftharpoons M^+NCO^- \qquad (13)$$

$$M^+NCO^-+NO \rightarrow M+N_2+O_2 \qquad (14)$$

yielding a surface isocyanate group, whiche ould be a possible intermediate of the catalytic reaction. Isocyanate species have been detected by infrared spectroscopy during the reaction of nitric oxide with carbon monoxide on the surface of noble metal catalysts[19,23] and also on supported CuO.[4]

The slowest step of the reaction of NO with CO is very probably the oxidation of active sites on the catalyst

. From the study of the interaction of the reacting mixture with the catalyst during the catalytic process, it appeared that the oxidation of CO with NO takes place on a weakly reduced surface (Fig. 5). As against that, the oxidation of CO with O_2 occurs on an oxidized surface, in agreement with the results of kinetic studies.[21]

In the case of SnO_2 containing Cr_2O_3, the catalytic reaction proceeded at a very low temperature, whereas pure SnO_2 did not exhibit any catalytic effect. We propose that the active catalytic sites in SnO_2+Cr_2O_3 catalyst are the lower valence (Cr^{3+}) ions located in the surface layer of SnO_2. As already shown these chromium centers can promote the chemisorption of NO and can be easily oxidized with NO to higher valence states. A possible driving force for this surface oxidation is that CrO_2 and SnO_2 both have rutil structure, and that CrO_2 is stabilized in the SnO_2 lattice. The slowest step of the catalytic reaction is the same as previously, i.e., the oxidation of reduced centers, as carbon monoxide reduces the higher valence chromium in a very fast reaction.[21] We assume that this redox mechanism also operates in the reaction of NO with other fuels.

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